CCSF PHYC 4D Lecture Notes

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Chapter 8
Many-Electron Atoms

Multiple particle wave functions

- In quantum mechanics, a system of particles is described by a wave function that depends on the position coordinates of each particle. For example, a two particle system is described by a wave function $\psi(\vec{r}_1, \vec{r}_2)$ that depends on the position vectors of the two particles.

- The probability of finding particle 1 within some volume $d^3\vec{r}_1$ around $\vec{r}_1$ *and* particle 2 within some volume $d^3\vec{r}_2$ around $\vec{r}_2$ is given by

$$P(\vec{r}_1, \vec{r}_2)\, d^3\vec{r}_1\, d^3\vec{r}_2 = |\psi(\vec{r}_1, \vec{r}_2)|^2\, d^3\vec{r}_1\, d^3\vec{r}_2$$

  The wave function should be normalized by integrating over *both* position vectors:

$$\iiint_{\text{spc}} d^3\vec{r}_1 \iiint_{\text{spc}} d^3\vec{r}_2\, |\psi(\vec{r}_1, \vec{r}_2)|^2 = 1$$

- If the motions of the two particles are independent of one another, then the two-particle wave function can be written as a product of two one-particle wave functions as follows:

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_1(\vec{r}_1)\psi_2(\vec{r}_2)$$

  In this case,

$$P_1(\vec{r}_1)\, d^3\vec{r}_1 = |\psi_1(\vec{r}_1)|^2\, d^3\vec{r}_1 \qquad P_2(\vec{r}_2)\, d^3\vec{r}_2 = |\psi_2(\vec{r}_2)|^2\, d^3\vec{r}_2$$

  each represents the probability of finding particles 1 and 2, respectively, within a certain small volume of space, independently of where the other particle is located. The single-particle wave functions should be normalized separately:

$$\iiint_{\text{spc}} |\psi_1(\vec{r}_1)|^2\, d^3\vec{r}_1 = \iiint_{\text{spc}} |\psi_2(\vec{r}_2)|^2\, d^3\vec{r}_2 = 1$$

  If the particles do not move independently, then the two-particle wave function cannot be written as a simple product.

- In any case, the spin states should also be included. The complete two-particle state would be given by

$$\psi = \psi(\vec{r}_1, \vec{r}_2)\chi_1\chi_2$$

or linear combinations thereof, where χ_1 and χ_2 are the spin states for particles 1 and 2, repectively. Once again, the wave function for two independently moving particles factors:

$$\psi = (\psi_1(\vec{r}_1)\chi_1)(\psi_2(\vec{r}_2)\chi_2)$$

- The momentum operators are given by

$$\hat{\vec{p}}_1 = \frac{\hbar}{i}\vec{\nabla}_1 \qquad \hat{\vec{p}}_2 = \frac{\hbar}{i}\vec{\nabla}_2$$

where $\vec{\nabla}_1$ and $\vec{\nabla}_2$ are derivatives with respect to $\vec{r}_1$ and $\vec{r}_2$, respectively.

- Plugging these operators into the classical expression for total energy yields the Hamiltonian

$$\hat{H} = \frac{\hat{p}_1^2}{2m_1} + \frac{\hat{p}_2^2}{2m_2} + U(\vec{r}_1, \vec{r}_2) = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + U(\vec{r}_1, \vec{r}_2)$$

and so the time-independent Schrodinger equation becomes

$$-\frac{\hbar^2}{2m_1}\nabla_1^2\psi - \frac{\hbar^2}{2m_2}\nabla_2^2\psi + U(\vec{r}_1, \vec{r}_2)\psi = E\psi$$

- If the particles do not interact with each other, then the potential energy function is separable

$$U(\vec{r}_1, \vec{r}_2) = U_1(\vec{r}_1) + U_2(\vec{r}_2)$$

In that case, the stationary states are product states:

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_1(\vec{r}_1)\psi_2(\vec{r}_2)$$

and each particle moves independently of the other. Each single particle wave function satisfies its own Schrodinger Equation

$$-\frac{\hbar^2}{2m_1}\nabla_1^2\psi_1 + U_1(\vec{r}_1)\psi_1 = E_1\psi_1$$

$$-\frac{\hbar^2}{2m_2}\nabla_2^2\psi_2 + U_2(\vec{r}_2)\psi_2 = E_2\psi_2$$

The energies add together

$$E = E_1 + E_2$$

- If the particles do interact, but the interaction is weak, then the product states may be approximate stationary states of the system. However, if the interactions are very strong, then the product states may be meaningless.

- This discussion can be generalized to an N-particle system. The wave function is a function of N position vectors

$$\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$$

The time-independent Schrodinger equation is given by

$$-\sum_{i=1}^{N} \frac{\hbar^2}{2m_i} \nabla_i^2 \psi + U(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)\psi = E\psi$$

If the particles are non-interacting, then the particles move independently of one another, and the stationary states for the N-particle system can be written as products of individual states

$$\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \psi_1(\vec{r}_1)\psi_2(\vec{r}_2) \ldots \psi_N(\vec{r}_N)$$

each satisfying its own Schrodinger Equation

$$-\frac{\hbar^2}{2m_i} \nabla_i^2 \psi_i + U_i(\vec{r}_i)\psi_i = E_i\psi_i$$

and

$$E = E_1 + E_2 + \ldots + E_N$$

Identical particles

- Suppose we perform an experiment in classical physics involving a red ball and a blue ball. Both balls have the same mass, size, shape, elasticity, etc. Surely we would be able to tell the two balls apart during the experiment, even though they have the same physical properties.

- What if both balls were blue? We should still be able to distinguish them (as long as we are careful), especially if the two balls remain physically separated during the experiment.

- What happens, though, if we perform an experiment with two electrons? Can we distinguish them? Well, if we painted one of them blue and the other one red, then yes, very easily. But we can't paint electrons. What if we carefully keep them separated? The uncertainty principle makes that impossible. No matter what barrier we place between the two electrons to keep them apart, there is always some chance that the two electrons will be able to tunnel through that barrier and change places without anyone knowing about it.

- In quantum mechanics, identical particles are *indistinguishable* and the two-particle wave function must reflect that fact. It should not matter if particle 1 is located at $\vec{r}_1$ and particle 2 is located at $\vec{r}_2$, or vice versa. The probability densities in either case must be the same. Thus, the wave function must satisfy

$$|\psi(\vec{r}_2, \vec{r}_1)|^2 = |\psi(\vec{r}_1, \vec{r}_2)|^2$$

This implies

$$\psi(\vec{r}_2, \vec{r}_1) = \pm\psi(\vec{r}_1, \vec{r}_2)$$

The wave function must either be symmetric $(+)$ or antisymmetric $(-)$ with respect to particle exchange.

- It turns out that the choice between symmetric and antisymmetric wave functions is not arbitrary, but depends on the spin of the particle.

  - Particles with integral spin (i.e., $s = 0$, 1, 2, ...) are called *bosons* and require symmetric wave functions. Photons, gravitons, and all mesons (including π) are examples of bosons.
  - Particles with half-odd-integer spin (i.e., $s = \frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$, ...) are called *fermions* and require antisymmetric wave functions. Electrons, protons, neutrons, quarks, and other leptons and baryons are examples of fermions.

- Composite particles (particles that consist of other particles) are fermions or bosons depending on how many fermions they contain. A composite particle containing an *even* number of fermions will behave as a boson (e.g., mesons are quark-antiquark pairs, and are thus bosons). A composite particle containing an *odd* number of fermions will behave as a

fermion (baryons are 3-quark combinations, and are thus fermions). The number of bosons contained by the composite particle is not relevant. This is all related to the way that individual spins of the constituent particles combine to form the overall spin of the composite particle.

- Recall that if two particles are not interacting, then the stationary states for the two-particle system are products of stationary states of the individual particles:

$$\psi(\vec{r}_1, \vec{r}_2) = \psi_a(\vec{r}_1)\psi_b(\vec{r}_2)$$

If the particles are identical, these product states may not have the required symmetry. In such cases, we need to combine product states appropriately in order to get the proper symmetry:

$$\psi(\vec{r}_1, \vec{r}_2) = \begin{cases} C(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) + \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)) & \text{bosons} \\ C(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)) & \text{fermions} \end{cases}$$

The constant C is for normalization, and usually equals $1/\sqrt{2}$ if ψ_a and ψ_b are distinct stationary states.

- Consider the example of two electrons, one in state ψ_a and one in state ψ_b. According to the simple product state above, electron 1 is in state ψ_a and electron 2 is in state ψ_b. But if the electrons are identical, then how do we know it isn't the case that electron 2 is in state ψ_a and electron 1 is in state ψ_b? The answer is that we don't: we must include both possibilities in the wave function.

- What happens to the above analysis if $\psi_a = \psi_b$. Is it possible to produce a combination of product states that represents both particles occupying the same state, ψ_a? The answer depends on whether the particle is a boson or a fermion.

- For bosons, there is no problem.

$$\psi(\vec{r}_1, \vec{r}_2) = C(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) + \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)) = 2C\psi_a(\vec{r}_1)\psi_a(\vec{r}_2)$$

In fact, if we choose $C = \frac{1}{2}$, we recover the simple product state which had the correct symmetry to begin with.

- For fermions, there is a problem.

$$\psi(\vec{r}_1, \vec{r}_2) = C(\psi_a(\vec{r}_1)\psi_b(\vec{r}_2) - \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)) = 0$$

It is not possible to construct a two-particle wave function for two fermions occupying the same individual state. *Two fermions cannot occupy the same state at the same time.* This is known as the Pauli exclusion principle, and plays a major role in multiple electron atoms. Since electrons are fermions, no two electrons can occupy the same atomic state.

- All of this can be generalized to N identical particles. The N-particle wave function $\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$ must either be symmetric (boson) or antisymmetric (fermion) with respect to particle exchange between *any two particles* in the system.

$$\psi(\ldots, \vec{r}_j, \ldots, \vec{r}_i, \ldots) = \pm\psi(\ldots, \vec{r}_i, \ldots, \vec{r}_j, \ldots)$$

- Product states can be combined to produce a wave function with the proper symmetry by summing over all possible permutations of the N particles.

$$\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = C\sum_p \alpha_p \psi_{p(1)}(\vec{r}_1)\psi_{p(2)}(\vec{r}_2)\ldots\psi_{p(N)}(\vec{r}_N)$$

For bosons, $\alpha_p = +1$ for all permutations. For fermions, $\alpha_p = +1$ for even permutations (even number of exchanges) and $\alpha_p = -1$ for odd permutations (odd number of exchanges). The fermion wave function can also be written as a determinant.

- For example, the properly symmetrized wave function for a three particle system would be given by

$$\psi = C(1_a 2_b 3_c + 1_b 2_c 3_a + 1_c 2_a 3_b \pm (1_a 2_c 3_b + 1_b 2_a 3_c + 1_c 2_b 3_a))$$

where 1_a is shorthand for $\psi_a(\vec{r}_1)$, etc. In the fermion case, this combination can be written as a determinant:

$$\psi = C \det\begin{pmatrix} 1_a & 1_b & 1_c \\ 2_a & 2_b & 2_c \\ 3_a & 3_b & 3_c \end{pmatrix}$$

- The Pauli exclusion principle also applies to N-particle systems. No two fermions can occupy the same state within an N-particle system. Examining the formula above for the 3-particle fermion wave function, if any two of the states were identical, the determinant would vanish because the matrix would have two identical columns.

- It should be noted that we have suppressed the spin states in the discussion above, but that spin needs to be included. When two particles are exchanged, their spin states should also be exchanged. The Pauli exclusion principle prohibits two or more identical fermions from occupying the same spatial *and spin* state.

- Summary of properties of bosons and fermions:

	bosons	fermions
spin	integer $(0, 1, 2, \ldots)$	integer $+ \frac{1}{2}$ $(\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots)$
wave function	symmetric	antisymmetric
Pauli exclusion	no	yes
examples	photon, graviton, gluon, all mesons (including π)	electron, proton, neutron, quark, all leptons and baryons

Many electron atoms

- The potential energy function for an N-electron atom with a nucleus of charge $+Ze$ located at the origin is given by:

$$U(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = -\sum_{i=1}^{N} \frac{Ze^2}{4\pi\epsilon_0 |\vec{r}_i|} + \sum_{i=1}^{N} \sum_{j=i+1}^{N} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|}$$

The first sum represents interactions between the electrons and the nucleus and the second (double) sum represents interactions among the electrons themselves. In principle, one can plug this into the Schrodinger Equation and solve for the N-electron wave functions.

- In practice, this is impossible to solve analytically even with $N = 2$. Numerical solutions exist, but they are difficult to calculate. Nevertheless, there is a lot we can say about many-electron atoms.

- In spite of the strong interactions among the electrons themselves, we can approximate the N-electron wave function as a product wave function. In a sense, we can think of each electron separately as belonging to a given single-electron state that is well described by the quantum numbers n, l, m_l, and m_s satisfying the same conditions as in the hydrogen atom. However,

- The energies of these states are not the same as the hydrogen atom (or hydrogen-like atom with a nuclear charge of $+Ze$). In fact, the energies now depend on l as well as n.

- The wave functions are likely to be different as well.

- The Pauli exclusion principle plays a significant role in the description of multiple electron atoms. Electrons are fermions, and so only one electron may occupy a given single-electron state. These states tend to fill up in order of lower energy to higher energy, so one subshell tends to fill before other subshells are started.

- Recall that when $l > 0$, there is some angular dependence associated with any one single-electron state. However, the electron density associated with electrons in a given *filled* subshell will be spherically symmetric, even if $l > 0$. One explanation that can be given for this is that the *total* angular momentum (both orbital and spin) for a filled subshell is zero.

- Thus we can think of the atom as a positive point charge at the center surrounded by a spherically symmetric negative charge distribution. Each electron in the atom interacts with this spherically symmetric charge distribution.

- Of course, the presence of electrons in *unfilled* subshells breaks the spherical symmetry, and allows directional bonding to take place (see Chapter 9). The spherical symmetry is still a good approximation, however, since there are only relatively few electrons in unfilled subshells.

- The interaction between an electron and a spherically symmetric charge distribution can be understood by using Gauss' Law. The electrical force experienced by any given electron at radius r will be due to the charge enclosed by a sphere of radius r. Electrons closer to the nucleus than r will contribute a negative charge that partially cancels the positive charge from the nucleus, reducing the "effective charge" of the nucleus as seen by the given electron. This effect is known as *screening*. Other electrons that are farther out than r will have no effect on the given electron and will not contribute to screening. Note that as r increases, more electrons are involved in screening and the effective nuclear charge is reduced.

- It follows that electrons occupying the inner (low n) shells will experience a strong attraction to the nucleus and be very tightly bound to it. The electrons occupying the outer shells of the atom will be screened by these inner electrons, and will experience a reduced effective charge. The effective charge seen by the valence electrons can be quite small (typically just a few times e).

- For a given n, lower l subshells have lower energies than higher l subshells. The reason for this is that electrons occupying lower l subshells spend more time closer to the nucleus where they experience a larger effective positive charge (less screening).

The periodic table

- The periodic table was originally set up by Mendeleev in 1859 (long before quantum theory) in order to explain the chemical behavior of the different elements. Each column represented elements with similar properties.

- As we consider atoms containing more and more electrons, the subshells fill in the order given below. Note the reversal of ordering between $3d$ and $4s$, $4d$ and $5s$, and $4f$ and $6s$, among others. Each row in this table corresponds to one row in the periodic table.

$$1s^2$$
$$2s^2, 2p^6$$
$$3s^2, 3p^6$$
$$4s^2, 3d^{10}, 4p^6$$
$$5s^2, 4d^{10}, 5p^6$$
$$6s^2, 4f^{14}, 5d^{10}, 6p^6$$
$$7s^2, 5f^{14}, 6d^{10}, 7p^6$$
$$\cdots$$

- Note: Fig. 8.1 (p. 228[238]) is *not* the correct energy level diagram for any particular electron, in the sense that electronic states that are far above or below the valence level will be very different from what the

diagram indicates. Each level is placed on the diagram with the assumption that the lower energy levels are (almost) completely filled and the current level is not.

- The order that the states fill up *within* a given subshell is not completely arbitrary. The capacity of a given subshell (n, l) is $2(2l + 1)$. The first $2l + 1$ electrons added to the subshell go into states with different values of m_l. These electrons are considered *unpaired* electrons because the corresponding electronic state with the same n, l, m_l but opposite m_s is empty. As electrons are added beyond the initial $2l + 1$, those electrons will pair up with the electrons already present in the subshell, until the subshell is completely full and all electrons are paired. Furthermore, the spins of the unpaired electrons tend to "line up". For the high capacity d and f subshells, the total spin of the atom can be quite high, as high as $s = \frac{5}{2}$ for d subshells and $s = \frac{7}{2}$ for f subshells.

- Section 8.4 goes into extensive detail of the properties of various elements:

  - Atomic radius vs. Z (Fig 8.3). Trend is that the radius spikes upwards when a new shell is started, and then gradually decreases as that shell is filled. The increase in the positive charge of the nucleus accounts for the gradual decrease of the atomic radius as the electrons are drawn in closer.

  - Ionization energy vs. Z (Fig 8.4). Trend is that the ionization energies tend to be lower when shells are starting to fill, as the valence electrons are very loosely bound in that case, and then gradually increase as the shell fills. *Nature prefers filled shells over unfilled shells.*

  - Resistivity vs. Z (Fig 8.5). I don't see a discernable trend, even though the book seems to claim that there is one. Electrical conduction has much more to do with how each of the atoms combine with all of the other atoms in a given solid. This will be addressed in Chapter 11.

  - Magnetization vs. Z (Fig 8.6). Here the trend seems to be higher magnetizations towards the middle of the periodic table where there are more unpaired electrons, and each electron has a greater angular

momentum. This is further enhanced by the fact that the spins of unpaired electrons tend to line up. All of this contributes to the overall magnetic dipole moment of the atom, which can be quite high in the middle of the transition metals as well as the Lanthanide and Actinide series.

Atomic spectra

- Recall that when electrons make a transition from a higher energy state E_i to a lower energy state E_f, the atom emits a photon whose energy makes up the difference:

$$\frac{hc}{\lambda} = h\nu = -\Delta E = E_i - E_f$$

This is as true for many electron atoms as it is for single electron atoms. The frequency of the emitted photon depends on the energy levels involved in the transition.

- When electrons make a transition into the very tightly bound lower energy levels, the emitted photons tend to be in the X-ray spectrum. Of course, such levels are usually filled, but they can be vacated by bombarding the atoms with high energy electrons (or other particles) — usually tens of kilovolt accelerating voltages are required.

- If we consider the transition from $2p$ to $1s$ in an atom with atomic number Z, the effective nuclear charge felt by the transitioning electron in each level is about $+(Z-1)e$ (only the one remaining electron in the $1s$ subshell is involved in screening). The photon energy is given (approximately) by

$$h\nu = -\Delta E \approx (1 - \tfrac{1}{4})(Z-1)^2 E_0$$

The atomic number Z can be determined experimentally this way, and was done by Moseley in 1913. He was able to make some corrections to the periodic table as a result.

- More typical transitions involve the valence energy levels. The photons emitted tend to be in or near the visible spectrum. The emission spectrum can be understood by studying the energy level diagram of the atom.

- Figs. 8.4[8.10] and 8.5[8.11] (p. 234[252]) of the textbook show the energy level diagrams for lithium, sodium, and helium. Fig. 8.17[8.13] (p. 248[257]) shows a more complete diagram for helium which takes into account the spins of the two electrons.

- Note that the electronic states are labeled by the complete electronic state (all electrons), although only the valence electrons are actually listed in the diagrams in the book. The reason for this is that the inner core electrons require much greater energies to excite than the valence electrons, so they normally stay in place.

- Normally the transitions involve a single electron moving from one single-electron state to another. Such transitions must obey the selection rules for a single electron:

$$\Delta l = \pm 1 \qquad |\Delta m_l| \leq 1$$

Note that all of the transitions shown in Figs. 8.4[8.10] and 8.5[8.11] satisfy these rules. In addition, there are selection rules for the total orbital and spin angular momentum L and S, namely:

$$|\Delta L| \leq 1 \qquad \Delta S = 0$$

- With all these selection rules, it seems likely that some of the excited states of an atom may not be able to make transitions to *any* lower energy states, at least not by any transition that satisfies all of the selection rules. Such states tend to have long lifetimes, and are thus called *metastable* states. An example would be the $1s^1 2s^1$ state(s) of helium.
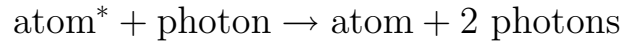
Lasers

- There are three mechanisms by which radiation can interact with an atom (asterisk indicates a higher energy (excited) state):

    - Spontaneous emission:

$$\text{atom}^* \rightarrow \text{atom} + \text{photon}$$

– Absorption:
$$\text{atom} + \text{photon} \rightarrow \text{atom}^*$$

– Stimulated (or induced) emission:
$$\text{atom}^* + \text{photon} \rightarrow \text{atom} + 2 \text{ photons}$$

- In each case, the photon energy equals the difference between the higher energy and lower energy atomic state. In the case of stimulated emission, the two photons emitted are *identical* in terms of energy (and thus frequency), polarization, direction of travel, and phase. Fig. 8.19[8.15] (p. 249[258]) in the textbook depicts these transitions.

- If there is an entire array of atoms in a given excited state, it is possible to create a cascade effect, where one photon induces emission from one of the atoms, causing two photons to come out, and then those two photons each induce emission from two other atoms, for a total of four photons, and so on. Fig. 8.20[8.16] (p. 249[258]) illustrates this cascade effect.

- A laser (Light Amplification by Stimulated Emission of Radiation) is a device that takes advantage of this cascade effect to produce an intense, perfectly monochromatic, coherent beam of radiation. Usually the beam bounces back and forth between two mirrors several times (in order to take maximum advantage of this amplification effect) before being released.

- A laser is normally designed to operate with two specific states of a given atom. The stimulated emission resulting from an induced transition from the higher energy state to the lower energy state yields the desired laser beam. This particular transition is known as the *lasing transition* (illustrate by drawing energy levels for some hypothetical atom, and picking out a particular transition).

- In order for the laser to function properly, two things must be true:

  – At any given time, the number of atoms in the higher energy state of the lasing transition must be greater than the number of atoms in the lower energy state. This is known as *population inversion.* When a photon of the correct energy approaches an atom in either

state, the atom will absorb the photon if it is originally in the lower state, and the atom will undergo stimulated emission if it is in the higher state. We want more stimulated emission than absorption, or else the number of photons will *decrease* over time.

– The transition rate for spontaneous emission between the two states of the lasing transition needs to be low enough, so that spontaneous emission does not contaminate the beam. Otherwise, the beam will not be coherent or unidirectional (it may also fail to be monochromatic because of Doppler broadening). Basically, we want a laser beam that is initiated by *one* spontaneously emitted photon, so that all photons in the beam are copies of that one photon.

- One of the keys to a functioning laser is using a lasing material which possesses a *metastable state*, which can serve as the high energy state for the lasing transition. Not only does this significantly reduce the chances of spontaneous emission from that state, but it also facilitates population inversion by allowing electrons that have been pumped up to the higher energy level via some *pumping mechanism* to stay there.

- Note that if the lasing material were to reach thermodynamic equilibrium, then the relative population of the higher and lower energy states is given by:
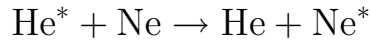$$N_{\text{high}}/N_{\text{low}} = e^{-\Delta E/kT}$$
where ΔE represents the (positive) energy difference between the two states. This implies that $N_{\text{high}} < N_{\text{low}}$: there are normally fewer atoms in the higher energy state. Population inversion requires continual pumping to maintain.

- One obvious idea is to use a metastable state, such as the $1s^1 2s^1$ metastable state of helium. The lasing transition would be the transition from that state to the ground state. One could imagine pumping electrons by using photons of the correct energy to excite electrons from the ground state directly to the metastable state. If one pumps electrons faster than they spontaneously decay, then it should be possible to maintain the necessary population inversion and generate the laser beam.

- The problem with this particular idea is that the lasing transition is, by definition, a difficult one to induce. The same selection rules which make

it difficult for the metastable state to decay to the lower energy state also make it difficult for the atom to absorb a photon and transition from the lower energy state into the metastable state.

- One improvement is to use a three-state mechanism, such as depicted in Fig. 8.21[8.17] (p. 250[259]) in the textbook. In that case, the lasing material is bombarded with a stream of electrons or EM radiation (at the correct frequency) which has the effect of bringing the atom from its ground state (1) to an excited state (3). That excited state then decays quickly to the metastable state (2). The transitions $1 \rightarrow 3$ and $3 \rightarrow 2$ both happen quickly, thus allowing for the population inversion between 2 and 1. The first laser, constructed by T. H. Maiman in 1960 using a solid ruby rod as the lasing material, is of this form.

- An even better idea is to use a four-state mechanism, such as depicted in Fig. 8.22[8.18] (p. 250[259]). In that case, electrons are pumped $1 \rightarrow 4$, which is immediately followed by a decay $4 \rightarrow 3$. The lasing transition is $3 \rightarrow 2$ (3 is metastable). Once the lasing transition occurs (hopefully by stimulated emission), the transition back to the ground state $2 \rightarrow 1$ happens very quickly.

- The main advantage of the four-state mechanism over the three-state mechanism is that the ground state is not part of the lasing transition. Once the atom makes it back to the ground state, it can no longer absorb a photon from the laser beam. The population inversion between 3 and 2 is easier to maintain since 2 is not the ground state.

- The He-Ne laser uses a variant of the four-state mechanism. Fig. 8.23[8.20] (p. 251[260]) in the textbook shows the energy level diagrams involved. The lasing transition is a Ne transition $2p^5 5s^1 \rightarrow 2p^5 3p^1$ ($+20.66\,\text{eV}$ and $+18.70\,\text{eV}$ above ground state, respectively), which corresponds to $632.8\,\text{nm}$ wavelength photon emission. Shortly after reaching $2p^5 3p^1$, Ne will decay back to the ground state $2p^6$ (with an intermediate step $2p^5 3s^1$).

- Interestingly, the $2p^5 5s^1$ state of Ne is *not* metastable. Population inversion is instead achieved by the fact that He (which makes up about 90% of the mixture) has a metastable state $1s^1 2s^1$ which has an energy of

+20.61 eV above ground state. When such a helium atom collides with neon in the ground state, the two atoms exchange excitation energy:

$$\text{He}^* + \text{Ne} \rightarrow \text{He} + \text{Ne}^*$$

These collisions keep the $2p^5 5s^1$ Ne state well-populated.

- Note: I can certainly see how the population inversion is maintained in the He-Ne laser by the collision mechanism described above. What is less clear to me is how contamination by spontaneous emission is avoided. There is no selection rule that forbids Ne:$2p^5 5s^1 \rightarrow 2p^5 3p^1$, so I would imagine the transition rates for such emission to be rather high.

- Lasers in general are not very efficient in terms of energy output (efficiencies are typically 0.001%–0.01%). A great deal of energy is used in maintaining the population inversion. What is gained by lasers is the fact that the beam is monochromatic, coherent, and (to within diffraction limits) uni-directional, and thus highly focussed. Total output power may be small, but the intensity (power/area) of the beam can be very large.

Some thoughts on spontaneous emission

- We have been discussing spontaneous emission for some time now. When an atom makes a transition from a higher energy state (E_i) to a lower energy state (E_f), a photon is emitted. One question we never addressed: how is this possible?

- Here's the problem: the atomic states that we have been referring to, including the ground state and all excited states, are supposed to be *stationary states*. They are energy eigenstates of the Hamiltonian operator. They oscillate at a definite frequency (related to the energy by the de Broglie relation $E = \hbar\omega$), and *they last forever*. Except now we are saying that they *don't* last forever. How is that possible?

- One explanation is that atoms are rarely found in isolation. Usually there are other atoms nearby. Or perhaps there may be stray electrons around. Or stray photons. Or some other particles or particle-like entities bouncing around. These stray interactions can change the dynamics

of the atom (which we had assumed was completely isolated) in such a way that the original atomic state is no longer a stationary state. A transition to a different (approximately) stationary state is quite possible in such cases.

- Transitions to *higher* energy states require a source of energy in just the right amount, and are unlikely to happen at random. But transitions to *lower* energy states can occur with the *emission* of a photon (or other particle) and are much more likely to happen.

- What if we completely isolate the atom? There is *nothing else around.* In this case, are all of the atomic states truly stable?

- It turns out, the answer is still *no,* for the simple reason that it is *impossible* to guarantee that there is *nothing* around. Remember that particles can be created by "borrowing" energy from the vacuum for short periods of time, in a manner consistent with the uncertainty principle

$$\Delta E \Delta t \geq \hbar/2$$

It is certainly quite possible that stray photons (or other particles) could be randomly created from the vacuum, disturb the atom, and cause it to make a transition to a lower energy state. To be sure, it is highly unlikely that this disturbance would cause a transition to a higher energy state (that would require borrowing a lot of energy, and it would have to be returned in a very short time anyway). But spontaneous transitions to lower energy states are quite possible.

- In fact, for transitions that obey the selection rules, there is mechanism (called dipole radiation) which turns out to be very efficient at inducing spontaneous emission. The transition rates are typically on the order of 10^8 Hz (corresponding to $\tau \sim 10^{-8}$ s). If the selection rules are violated, then other mechanisms for spontaneous emission still exist, but they are typically much less efficient, with transition rates as low as 10^3 Hz or less ($\tau = 10^{-3}$ s or longer).